Evaluation of the effect of size reduction and thermal treatment on metal extraction from PCBs of mother board and digital video drive of desktop PC

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The study aims at evaluating the effect of particle size and thermal treatment on printed circuit boards (PCBs) of Mother Board (MB) and DVD on metal extraction. Results show around 90–95% (w/w) and 35–40% (w/w) of total Al and Cu respectively, in CPU could be recovered by systematized disassembly. Remaining embedded Al and Cu require metallurgical or hydro-metallurgical processing. Cu extraction increases with size reduction. Thermal treatment of MB–PCB shows reduction in Cu extraction (23–38%) for all sizes in comparison without thermal treatment, while DVD–PCB showed surge in extraction after thermal treatment (41–141%) in comparison without thermal treatment.

Keywords: Copper, environment, E-waste, recovery, leaching.

ELECTRONIC industry is a dominant and fastest growing industry[1] of the 20th and 21st centuries. Electronic and electrical equipment (EEE) has dominated the lives of domestic and industrial users. Nevertheless, the primary disadvantages associated with EEEs is its ever flourishing quantum both in developed and developing countries; and hazardous materials such as PBR, Pb, As, Hg, Cr, Cd, halogenated substances, polychlorinated biphenyls, plastics, etc. present in it. Printed circuit boards (PCB), which are an essential component of almost all EEE, include brominated flame retardants (BFRs), etc., and could be extremely threatening to human health and environment, if not handled and treated properly. The continuous and rapid technological up-gradation and augmentation of new features, minimizes the previously estimated expectancy in terms of the average weight composition (kg)/average useful lifespan (years) of commonly used EEE (such as television (TV) – 24/10; personal computer (PC) – 27.2/5; refrigerator – 30/10; mobile phone – 0.12/3 and washing machine – 27/12)[2,3].

Further, discarded or waste EEE (WEEE) is a rich source of valuable (recoverable) materials such as plastic, Fe, Al, Cu, Ag, Au, Pd, etc., which has significant percentage share by weight and high economic value (Figures 1 and S1, see Supplementary Material online)[4,5]. Consequently, this attracts many informal and unorganized recyclers, generally who apply rudimentary technologies and processes, with sole intention to recover valuable materials and earn profit, leading to serious impact on environment and human health[6]. Especially in developing countries such as India, the new E-waste Rule, 2012 is in force for the safe collection, handling and treatment of the e-waste in the environment-friendly manner[7].

Furthermore, PCs are the dominant contributors to e-waste in developed as well as developing countries[8] and are a significant source of both hazardous and valuable materials. Basically, a desktop PC consists of three primary constituents: (a) central processing unit (CPU) (with fan, IC boards, DVD drive, CD drive, hard disk, shell casing, power supply, fan, etc.), (b) display monitor and (c) keyboard and mouse. Due to complex composition of PC, extensively physical dismantling is practised; however, further treatment for recovering valuable materials of high economic value from PCBs and ICs present in it is needed. Though precious and valuable metals in PCBs are only 1% by weight, they account for 80% of the total intrinsic value[9]. The composition of PCB is quite varied consisting of polymer (epoxy resin (EP) or phenollic resin, etc.) (50%), glass fibre (20%) and metals (30%) (20% Cu, 8% Fe, 4% Tn, 2% Ni, 2% Pb, 1% Zn, 0.2% Ag, 0.1% Au and 0.005% Pd)[10].

However, processing of waste PCBs (WPCB) is a challenge, as it is complex and diverse, in terms of type, size, shape, materials and component's make-up, and also of original equipment's manufacturing processes. Ordinarily followed processes such as open burning of PCBs for Cu and Fe recovery, produce dioxins and furans, due to the presence of BFR in the PCBs[10]. Bio-leaching and ammoniacal sulphate or chloride solutions were used previously to study the effect of shredded PCB particle size on Cu

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	Aluminium	Copper	Lead	Zinc	Nickel	Iron	Plastic	Glass	Silver	Gold
PC	3.0839	1.6961	0.0857	0.3598	0.0000	4.4545	1.2507		0.0050	0.0004
TV	0.4344	1.2308	0.0724	0.1086	0.0138	4.3440	9.4120	19.1860	0.0007	0.0004
Refrigerator	3.0839	1.6961	0.0857	0.3598	0.0000	4.4545	1.2507	0.0000	0.0050	0.0004
Mobile Phone		0.016							0.00035	0.000034

Figure 1. Per unit average weight of valuable and precious elements in EEE/e-waste.

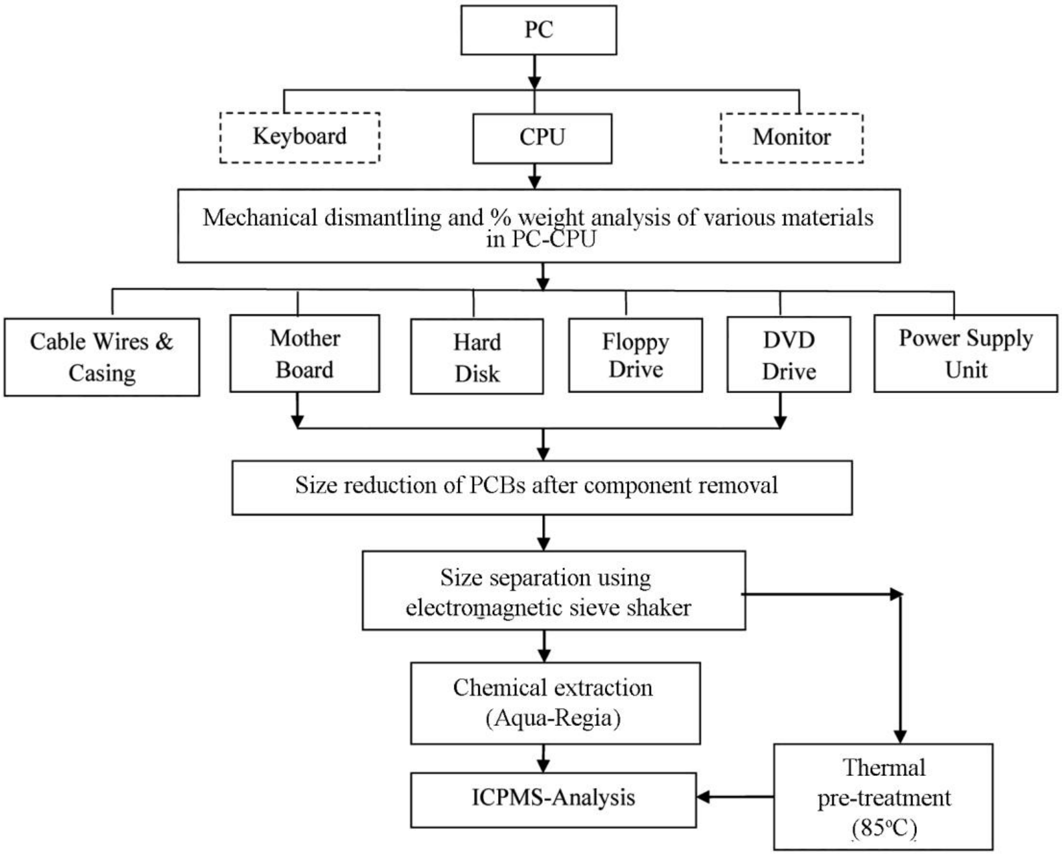

Figure 2. Flowchart showing the experimental procedure.

leaching[11,12]. However, a systematic comparative study involving various PCBs has not been reported to the best of our knowledge. In this regard, an environment-friendly process for extracting Cu and other metals from the WPCBs was studied. This research is primarily aimed at evaluating the effect of particle size reduction and thermal treatment to PCBs of Mother Board (MB) and Digital Video Drive (DVD) on metal extraction efficiency, by minimizing environmental and occupational impact, through volume reduction of the entire material to be processed for valuable materials recovery from CPU of PC.

Materials and methods

A discarded CPU (e-waste) (manufactured in 2004; 8 kg) collected from the stores of NEERI (National Environmental Engineering Research Institute, Nagpur) was utilized as the raw material for the experiment. The entire study has been broadly divided into three steps (Figure 2).

Pretreatment: preparation, comminution and separation

The pre-treatment process commences with systematic manual dismantling of the CPU using tools such as screwdriver, hammer, pliers, etc. Analysing the total content of valuable metals in a CPU serves two purposes: (1) identification of parts loaded with significant quantity of valuable materials; and (2) scrutinizing weight proportion of various components and parts. To enhance extraction efficiency, major parts such as hard disk, DVD drive, floppy drive, power supply unit, MB, etc., and components (such as transistors, batteries, diodes, capacitor, USB ports, etc.) in that individual part were identified and sorted. Precise weight analysis of all separated parts was done to find out valuable (Al, Cu, plastics, etc.) and other materials (including hazardous) present in it, and was compared with the existing information available in the literature. Metals were disassociated from non-metals in order to minimize the quantum of material to be processed – to enhance the targeted material concentration; and facilitate further chemical processing – as metals and non-metals have divergent reaction chemistry.

Sample preparation through mechanical processing

Although the compositions of different units of PCs are different, many studies have revealed that PCBs contain maximum valuable and precious elements[13], hence the PCBs of sizable weight were selected for the experimentation purpose and comparative study.

Components such as ICs, transformers, fan, resistors, capacitors, pins, heat sink, motors, batteries, etc., mounted on the various PCBs were systematically and carefully detached using pliers and spanners, to minimize occupational and environmental impact arising out of the various hazardous materials present in it.

Furthermore, the bare PCBs (after removal of mounted components) were separately cut into size of 3 cm × 3 cm by pliers and further reduced using mortar pestle and laboratory mixer grinder. The crushed samples were subjected to electromagnetic sieve shaking in continuous and intermittent mode for 5 and 2 minutes respectively, for separating and determining the weight percentage distribution of the different size fractions. The study was performed to investigate the effect of size reduction on valuable material (Cu) recovery and thermal treatment on the leachability of the metals, as thermal treatment aids to remove the non-metallic element of the PCB resulting in higher effective dissolution. Li *et al.*[14] reported the advantages of thermal shock technique by virtue of variance in the physical performance of PCB material. However, no result has been reported regarding the effect of low-temperature thermal treatment on PCBs, and therefore an attempt has been made to study its effect on chemical extraction of valuable metals from PCB with minimum energy requirement. Accordingly, one part of the sample was directly chemically leached (non-thermally treated), whereas another was thermally treated in laboratory oven at 85°C for 6 h before leaching.

Chemical extraction of metals via leaching

A hydrometallurgical process which uses acidic and alkaline solutions for the dissolution of metals was applied to extract the metals from PCBs since these methods are more exact, predictable and easily controlled than the pyro-metallurgical processes for metal recovery from PCBs[15]. Moreover, temperature exercise in pyro-metallurgical processes leads to serious environmental complications, especially air pollution[16]. Aqua regia was utilized as it dissolves most of the metals[17] except Ag which has strong chemical durability. Non-thermally and thermally treated samples were treated with aqua regia; at 1 : 4 solid to liquid ratio; for 48 h duration at room temperature. After appropriate filtration and dilution, the metal concentrations were analysed by inductively coupled plasma optical emission spectroscopy (ICPOES) for metal concentration of various elements in leachate. Further, transformations in the morphological structure before and after treatment were studied using compound digital optical microscope.

Results and discussions

Pretreatment: preparation, comminution and separation

Figure 3 shows the evaluated material (Al, Cu, Fe, plastics, rubber, other (ceramics, glass, fibres, silica, precious elements, etc.)) composition by wt% of the five preeminent parts (DVD, floppy drive, hard disk, power supply unit and MB) found in the CPU. From the systematic and separate manual dismantling of CPU, it can be analysed as follows.

(1) About 90–95% (w/w) of the total Al was found in casings of DVD, floppy drive, hard disk and power supply unit. Specifically Al was employed in the base casing (250 g), fins (250 g), top cover (150 g), heat sink (75 g), spindle motor axis (45.61 g), platter (23.16 g), capacitor foils (29.6 g), north bridge (29.83 g), top cap and eject mechanism (23.54 g), outside metallic cover (14.08 g), spacer ring, various slots and ports, actuator arm, head stack assembly, etc. and can be conveniently recovered using facile mechanical tools, without causing any negative impact on environment and occupational health. The remaining 5–10% (w/w) Al (embedded in wire and PCBs) needs metallurgical or hydrometallurgical processes for recovery, which may have environmental implications.

(2) Approximately 35–40% (w/w) of Cu could be conveniently recovered from the Cu windings of motor, transformers, motor of various drives, etc. While 30–35% (w/w) was embedded in PCBs and 25–30% (w/w) in connecting wires and cables.

(3) Parts such as IDE, ICs, connector pins, south bridge, etc. are also significant sources of precious

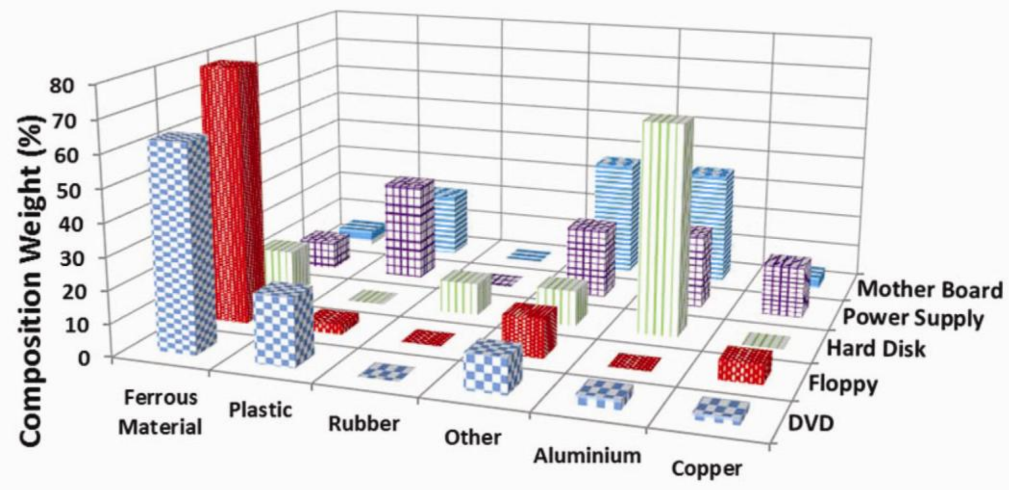

Figure 3. Per unit weight percentage of the materials from separated parts of CPU in PC.

Table 1. Weight percentage distribution in various size fractions

MB–PCB	Size (mm)	8	6	4	2	1	0.71	0.5	Fines
	Wt.%	27.14	38.45	28.55	1.49	2.41	0.96	0.24	0.75
DVD–PCB	Size (mm)	2	1	0.71	0.5	0.3	0.15	Fines	
	Wt%.	12.30	10.87	10.95	10.30	12.51	23.75	19.31	

materials (Au, Ag, Pd) along with Al, Cu and plastics. Therefore, systematic elimination and further processing of these parts are important from the environmental and economic recovery perspective.

(4) As hazardous materials are present in only few components, quantification and designation of the complete PC as a hazardous waste is inappropriate. The adopted treatment procedure can restrict cross-contamination and entry of hazardous material into the environment during recovery.

Sample preparation through mechanical processing

PCBs of MB and DVD have a sizable weight (Figure S2; see Supplementary Material online) and hence are preferred for further processing and comparative study. Table 1 shows the weight percentage distribution of MB–PCB and DVD–PCB in various size fractions after size reduction and sieving.

Furthermore, shredding and size reduction of the PCBs is a high-energy and time-consuming process[11], and it is difficult and uneconomical to reduce the size of all PCBs to <0.5 mm in practice, because of hardness and tenacity. Also, it is a heat-generating process; and the plastic-fibre glass material can agglomerate with metals complicating the grinding process. Pint-size fraction can cause various difficulties in processing and decreased leachability[11] and is generally rich in plastic materials only[18]. In MB–PCB, the presence of thermoplastic EP with fiber glass (Figure S3 *a*; see Supplementary Material online) (provided for extra tensile strength) makes size reduction difficult. However, DVD–PCB without glass fibre (Figure S3 *b*; see Supplementary Material online) was easily reduced in size.

Fourier transfer infra-red spectroscopy (FTIR) analysis of both PCBs was performed to determine the various functional groups predominantly present in the PCBs (Figure 4). FTIR analysis uses identification of absorption bands associated with the vibrations of functional groups in the brominated epoxy resins (BER). However, complex molecular structure of the laminates combined with the overlap of bond energies made it difficult to interpret the spectra by locating the exact wave numbers corresponding to the functional groups. FTIR library was prepared from the literature as shown in Tables 2 (refs 19, 21–23) and 3 (refs 21, 23–30) respectively, which clearly indicates the presence of different predominant functional groups.

Consequently (Figure 5), it is evident that chemical leaching increases with the diminution in sample size and vice versa, due to increase in surface area, enabling expanded exposure of metals, offering lesser mass transfer resistance by the EP layer, facilitating higher diffusion of leaching solvent and finally resulting in maximum dissolution of metals in solvent. Therefore, 2 mm fraction in MB–PCB has maximum metal concentration. Cu concentration is maximum, in comparison to other metals, in all size fractions and is predominantly higher, i.e. 34.18 g/kg

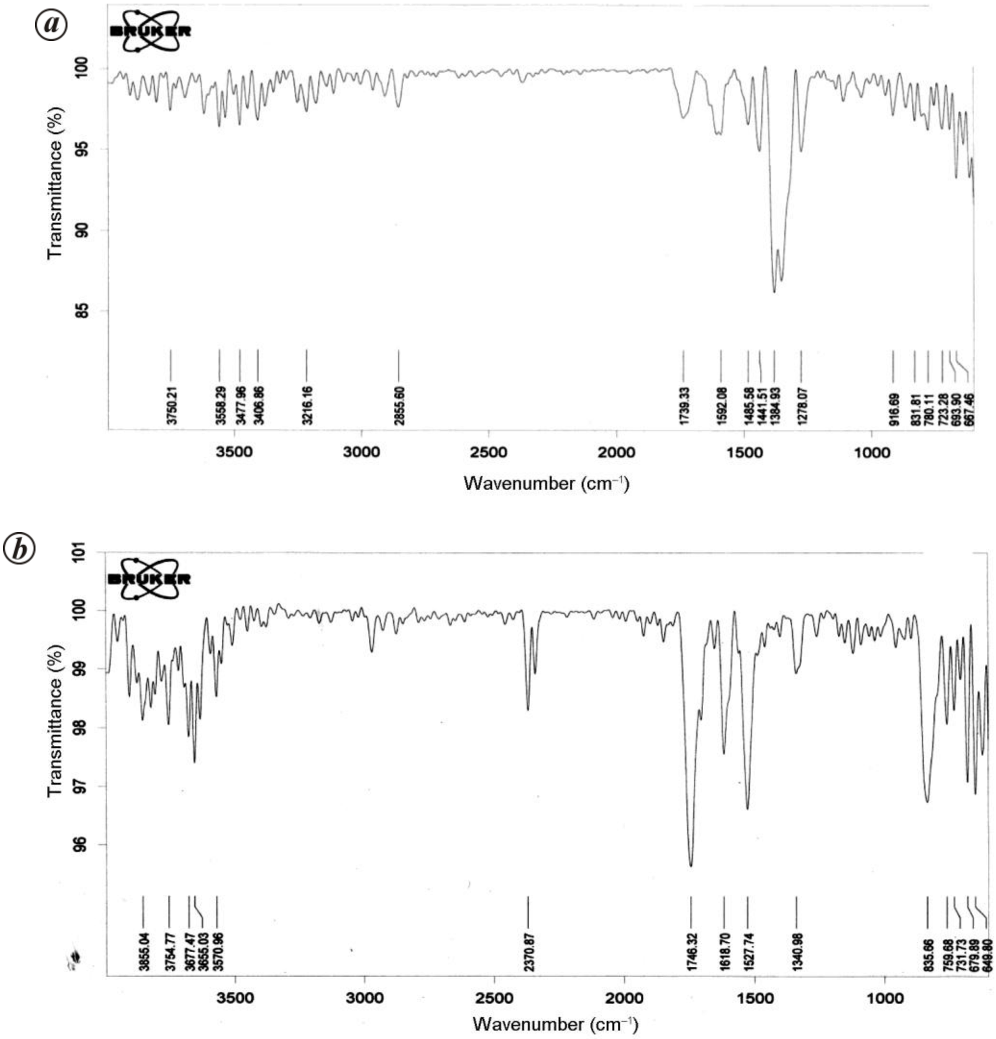

Figure 4. FTIR analysis of (***a***) DVD–PCB and (***b***) MB–PCB.

Table 2. Typical functional groups and wave numbers present in MB–PCB

Wave number (cm^{-1})	Functional group	Reference
3300–3600	O–H (alcohol)	21
3033	C–H; Methyl and methylene group	22
1746	C=O: Flame retardant C=O stretch	19
1619	C=C; alkene, aromatic ring	23
1528	Benzene ring	
1341	C–H bend: methyne	23
1241	P=O: Phenol of phenyl derivatives flame retardant	22
836	C–H: Benzene rings	22
760	C–C Vibration	23
732	$-CH_2$ Methylene	23

in the 2 mm fraction, in comparison with 4, 6 and 8 mm fractions which has 22.69, 20.03 and 21.31 g/kg, respectively; whereas in DVD–PCB, it is maximum (195.28 g/kg) for 0.3 mm fraction. Cu concentration is higher in the MB–PCB than in DVD–PCB. Fe content is higher in 2 mm fraction and pretreatment with magnetic separator can further enhance the Cu extraction efficiency. The optical microscopy (Figure S4; see Supplementary Material online) shows the leaching of embedded Cu.

Chemical extraction of metals via leaching and effect of thermal treatment

Figure 6 shows that in MB–PCB there is a comparatively converse effect of thermal treatment (at 85°C for 6 h) on the leaching of various metals in comparison with the non-thermally treated samples of all four sizes. There is diminution in the leaching of Cu for all sizes in the range 23–38% (approximately) and also of other metals. This finding is inconsistent with that of Masavetas *et al.*[20], where the optimum temperature for the leaching was 80°C.

Table 3. Typical functional groups and wave numbers present in DVD–PCB

Wave number (cm^{-1})	Functional groups	Reference
3750, 3558	Hydroxyl bond	21
3478, 3407	–OH or –NH_2: OH from opening of epoxy ring and –NH_2 from DICY curing agent	24
3217	–NH_2 and –NH: from BAP, TAM (phosphorus-containing-amine)	25
2856	–CH (From WSR-HPPE (EP with phosphorus flame retardant))	26
1740	–C=O (Carbonyl): From DICY-cured epoxy C=O (amides, ketones, aldehydes carboxylic acid, esters)	27
1591	Phenyl-P: From DHPDOPO (phosphorous-based flame retardant) phenyl-NH_2: From epoxy resin	28, 29
1486, 1592	Benzene ring	
1441	–CH_3: methyl C–H asymmetry	23
1385	–CH_3: Gem dimethyl	23
1278	P=O: From BPHPPO (phosphorus-based flame retardant)	30
916	CH_2–O–CH_2 : (epoxide ring) From EP monomer	27

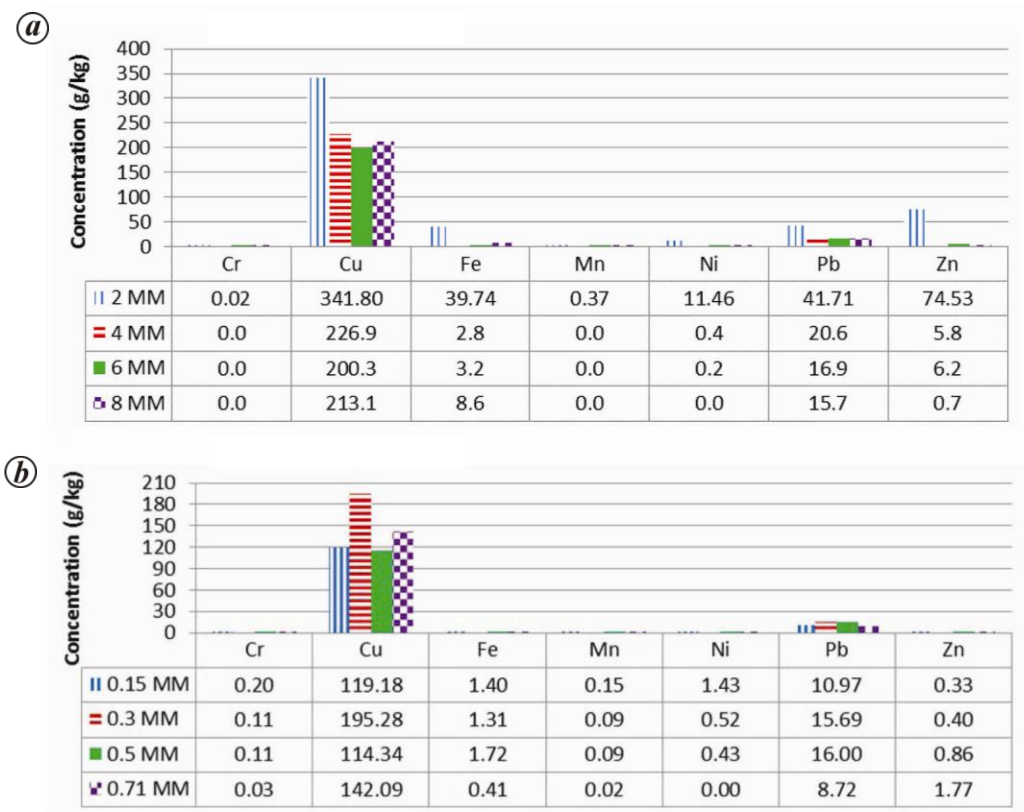

Figure 5. Effect of size reduction on the chemical leaching of various metals of (***a***) MB–PCB and (***b***) DVD–PCB.

Furthermore, MB–PCB is composed of glass fibre reinforced EP (Figure S3; see Supplementary Material online) with embedded Cu sheet, consequently which may change to glassy slag[11] on thermal heating and restrain the diffusion of solvent and dissolution of the metal. BER used in MB–PCB exhibits glass transition temperature (Tg) of around 130.12°C, which manifests the commencement of BER chain movement. However, heating below Tg leaves it frozen[19] leading to low Cu recovery due to minimal Cu and solvent interaction, in comparison to the non-thermal treatment.

However, thermal treatment of DVD–PCB enhances metal leaching in comparison with the non-thermally treated samples in all four size fractions as the composition of the DVD–PCB is distinct in comparison to MB–PCB as discussed previously. Further, there is surge in the Cu leaching for all size fractions in the range of 41–141% (approximately) as thermal heating results in thermal decomposition exposing metals which facilitates better solvent interactions leading to better Cu recovery. Thus, MB–PCB and DVD–PCB must be identified and processed distinctly for maximal valuable metal recovery.

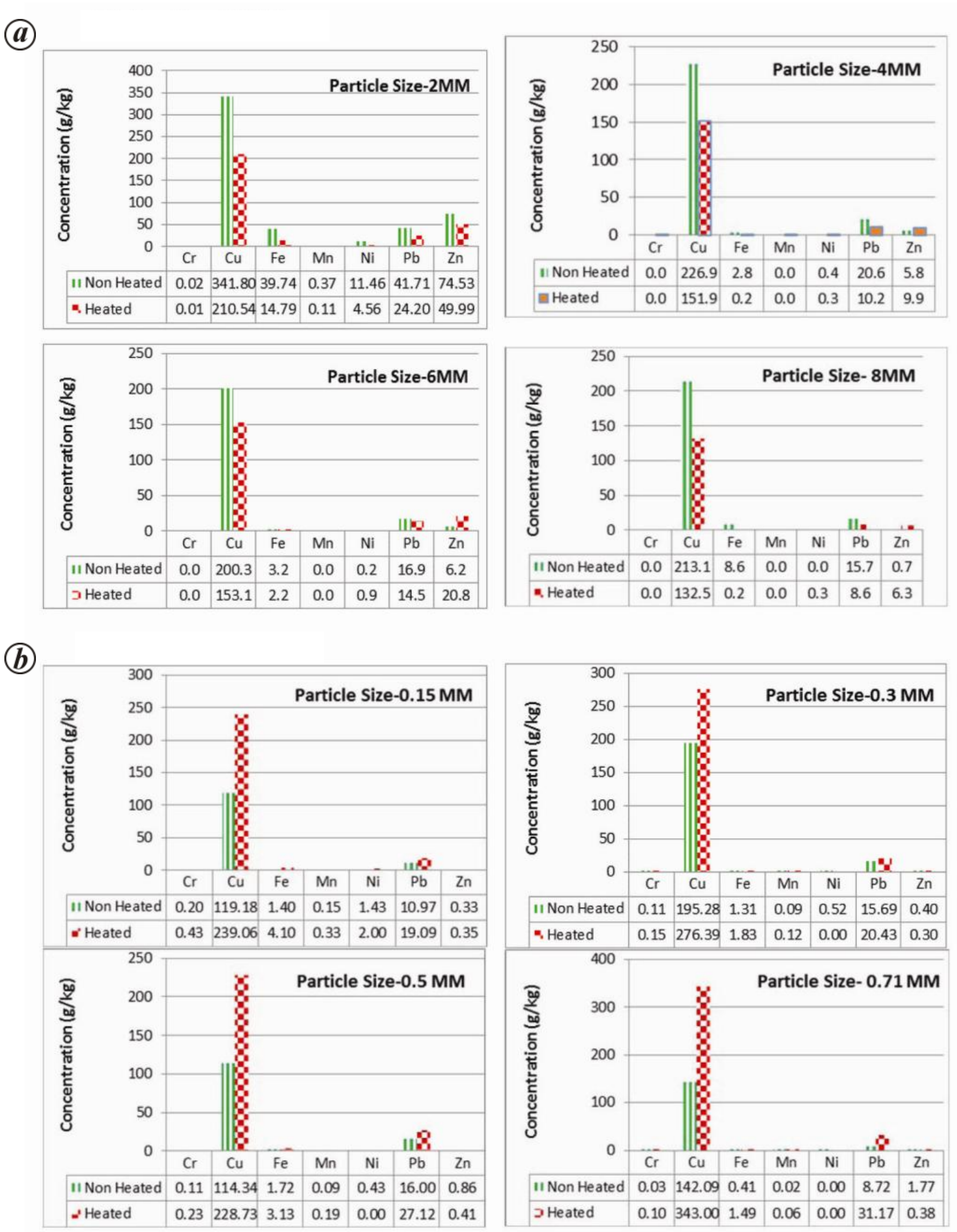

Figure 6. Effect of thermal heating on the leachability of valuable and toxic metals of (***a***) MB–PCB and (***b***) DVD–PCB.

Metallic copper can be recovered from the leaching solvent through electrodeposition in an electrolytic cell[20]. Purification of Cu by solvent extraction with organic LIX 26 and electro-winning can also be conducted to increase its purity[17].

Conclusion

The study revealed that, WEEE, especially PCBs could be a promising resource for the recovery of valuable metals. Systematic manual dismantling can conveniently recover 90–95% (w/w) of Al and 35–40% (w/w) of Cu present in CPU, and the remaining metals in the embedded form may require pyro-metallurgical or hydro-metallurgical processes. Manual dismantling may not be economical in developed countries where labour cost is formidable. It is definitely a favourable option in developing countries where labour is cheap and available and which may lead to employment generation[6]. Metal leaching was found to surge with particle size reduction, due to increase in surface area. Although DVD–PCB showed significant (41–141%) surge in metal leaching, MB–PCB shows no significant effect on thermal treatment, due to different material composition, indicating that MB–PCBs should be independently processed from other PCBs for efficacious valuable material recovery and ease of process operation. Further study and analysis of the MB–PCB and other PCBs in terms of their material composition is essential to investigate further recovery processing options.

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